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16. ABSTRACT

Research is being conducted to investigate closure methods for lagoons containing TNT and RDX wastes (pink water). Research has included (1) an evaluation of existing asphalt encapsulation techniques for hazardous wastes, (2) an evaluation of alternative heating/mixing systems, (3) review of the properties of various asphalt products that may be used, (4) laboratory experiments on the temperature and holding times required for thermal breakdown of the various compounds present in the sludge, and (5) preliminary design of a pilot mixer/heating system. A synthetic sludge with physical properties similar to the actual sludge will be used during the initial runs and during modifications of the pilot system. Actual lagoon sludge will be used in the field for the final testing. Results to date indicate that asphalt encapsulation of pink-water sludges using either a static or pug mill mixer appears to be a potential alternative to encapsulation by twin-screw extruders. Heating experiments of pink-water sludge not yet encapsulated indicated a 90% reduction in levels of explosive and nitroaromatic compounds at a temperature of 250°C.

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Research is being conducted by the USEPA to investigate closure methods for lagoons containing TNT wastes (pink water). Asphalt encapsulation, combining heating and mixing, is one process being considered for the treatment of a sludge containing trinitrotoluene (TNT), hexahydro-1,3-5-trinitro-1,3,5-triazine (RDX) and other nitroaromatics. The lagoon under investigation contains approximately 365 m^3 of sludge with up to 56,700 mg/kg TNT, 3740 mg/kg RDX and lesser amounts of other nitroaromatics and metals.

Asphalt encapsulation techniques, consisting of mixing heated asphalt with the sludge material, are being considered as a treatment option. Coating (or micro-encapsulation) of the sludge particles would improve the leachate quality and should act to reduce the reactivity of the explosive compounds by decreasing the propagation pathway of any reactions in the explosive compounds. Addition heating of the mixture should act to thermally degrade the nitroaromatic and RDX compounds in the sludge.

Research to date has included (1) an evaluation of existing asphalt encapsulation techniques for hazardous wastes, (2) an evaluation of alternative heating/mixing systems, (3) review of the properties of various asphalt products which may be used, (4) laboratory experiments on the temperature and holding times required for thermal breakdown of the various compounds present in the sludge and (5) preliminary design of a pilot mixer/heating system. A synthetic sludge with physical properties similar to the actual sludge will be used during the initial runs and during modifications of the pilot system. Actual lagoon sludge will be used in the field for the final testing.

Factors which are being evaluated include residence times required for both mixing and thermal breakdown, mobility of the system, safety considerations, batch vs. continuous designs, and through-put rates. Pre-

viously developed asphalt encapsulation procedures which could be mobilized would require excessive processing times and high capital costs for lagoons of this size. Use of ancillary processes, such as dewatering, and necessity for predrying of the sludge prior to encapsulation will also be evaluated.

INTRODUCTION

This research effort is directed at assessing the feasibility of using asphalt encapsulation to treat the sludge in a wastewater lagoon (Triegel and Kolmer, 1983), used in the past to dispose of TNT and RDX contaminated water resulting from the assembling, loading and packing of explosives ("pink water"). This work is being funded by the USEPA-MERL.

Site Conditions

The pink water lagoon under study is approximately 3500 m^2 in area and has been in existence since the late 1960s. Field measurements were made to determine the thicknesses and volumes of the sludge and wastewater in the lagoon. At the time of measurement, the water was approximately one meter deep and the sludge volume was estimated to be 365 m^3. It was found that the greatest thickness of sludge occurred very near the point of discharge of wastes into the lagoon, indicating rapid settling of coarser particulates in the water. Concentration distributions of several of the sludge constituents (tetryl, RDX and 2,4-Dinitrotoluene) were similar to the thickness contours, indicating a possible association of these compounds with the coarser particulates. The concentration of 2,4,6-TNT did not vary in a systematic manner with the sludge depths indicating a more uniform, non-size dependent distribution of the compound.

Chemical analyses of the groundwater, lagoon water, sludge, and soils underlying the lagoons were performed to identify the contaminants present and to characterize certain parameters which could affect the treatment process. These results are summarized in Table 1. Three monitoring wells were installed in addition to an existing well for long-term monitoring of the groundwater quality near the lagoon.

Process Selection

Asphalt encapsulation was considered as a treatment technique at the pink water lagoon since it has the potential to both thermally degrade as well as encapsulate the explosive and nitroaromatic compounds in the sludge. Asphalt encapsulation in this situation is the combining, heating, and mixing of asphalt and a waste material. It is not the coating of a monolithic block of waste with asphalt. Coating of waste particles with asphalt using twin-screw extruders has been used in the past, primarily for waste processing in the nuclear industry (Malone and Jones, 1980; Doyle, 1979). In this process, the asphalt and wastes are heated and mixed in the extruder, which serves the dual purposes of reducing waste particle size while mixing and coating the waste thoroughly with the asphalt. Coating of the pink water sludge particles should also reduce reaction propagation pathways and enhance the safety of the design. The temperature profile along the screws (several feet in length) can be closely controlled. The residence time in each section of the screw can be varied by changing the screw configuration and the speed of rotation. Water and volatile organics are evaporated and collected in a condensor system or removed under vacuum. The process generally results in a substantial volume reduction, due to the removal of water, and the treated product which is more resistant to weathering and cracking.

A vendor was contacted to evaluate the costs and feasibility of utilizing a twin-screw extruder as a mobil unit. Several factors were unique to this project which had not been critical in past waste encapsulation systems using the twin-screw extruder/asphalt system. These factors included (1) the need for a mobile system, (2) demonstration of the safety aspects prior to implementation so as to allow protection for personnel working with potentially reactive material, (3) heating requirements beyond that necessary to melt and mix the asphalt in order to enhance thermal degradation of nitro-aromatic compounds, and (4) possible extension of the system to treat larger volumes of contaminated soils that may be located beneath the lagoons. These considerations were in addition to the normal constraints of time required to process the wastes, costs of treatment, compatability of the wastes and asphalt, lack of undesirable by-products, and the suitability of the product in terms of stability and leaching characteristics.

After a preliminary evaluation, it was concluded that (1) a twin-screw extruder which was small enough to be mobile would require excessive (more than 1 year) through-put times for the pink water lagoon sludge, and (2) the cost of the equipment (rental or purchase) and the additional engineering time was too great for closure of only one lagoon. At this point, a feasibility study of alternative mixer systems was initiated by Foster-Miller Associates, Inc. This study included an evaluation of existing mixing equipment and asphaltic materials, an outline of the major process steps, and a heating experiment to determine the breakdown temperature and holding time for the nitroaromatics and RDX in the pink water sludge. The results of these investigations are described below.

Selection Criteria for Mixers and Asphalt Types

Since a wide range of both batch and continuous type mixing candidates was available for consideration, evaluation criteria were established to compare the relevant features. These criteria included:

- Degree of Mixing - Generally, how well does the equipment mix materials when used in its normal operating range for a nominal duration?

- Provisions for Loading/Discharging Materials - Does the mixer have loading chutes, discharge gates?

- Field Worthiness - Is it able to withstand over-the-road vibration? Resistance to elements as is? Ruggedness?

- Heat Capabilities - Is mixer equipped with a heat jacket, is it a standard option, or is a separate design required?

- Sludge Consistencies - Can it be loaded and used at all ranges of sludge water content from slurry to dried mud?

- Portability - Can it be taken over-the-road in terms of weight and size? Is it compact in design. Can it fit on one truck trailer?

- Cost - This includes the driving power, motors, pumps, etc.

- Overall Complexity - Can it be operated with minimum worker training? Number of working parts? Does it require specialized service

technicians? Are replacement parts difficult to locate?

A number of mixer candidates was considered for use. Some types of mixers are very similar and were considered as a group, i.e., vertical axis mixers. The candidate types are described in Table 2. The mixer candidates were then evaluated using the criteria outlined above. Table 3 provides a summary matrix of each mixer and evaluation criterion.

The mixer selection matrix produced two potentially favorable candidates. These are the pug mill and the static mixer. Since neither of these two candidates has been used for the subject encapsulation process, it is difficult to compare their anticipated performance. However, each has a few general advantages and disadvantages described as follows.

Mixer	Advantages	Disadvantages
Pug mill	o proven construction worthy machinery	o large, heavy machinery
	o high degree of of mixing	o requires large power drive
	o minimal design change for use	o more expensive option
Static	o inexpensive	o requires pump to drive materials through mixer
	o no moving parts	o sharp increases in asphalt viscosity at cooler temps may cause problems
	o can be used to transfer heat to sludge	o greater design cost
	o extremely compact portable	
	o easy to simulate on a pilot scale	

As part of the effort to identify mixing methods, a survey of the common asphalt grades was investigated. Table 4 shows these asphalt types and their properties. The information most pertinent to mixing is the viscosity properties and flash points of the asphalts. These parameters help identify mixing energy requirements and safe operating temperatures.

Preliminary Design of the System

The major steps of the encapsulation process are shown in Figure 1. The raw sludge would be transported from the pond through a classifier which may take the form of a screen or grizzly to prevent oversize and foreign objects such as wood and cobbles from entering the system. The material would then proceed to pretreatment such as dewatering by filters, centrifuges, or heating, or, it may be deposited directly into a surge tank to await feeding to the mixer. The advantages of heating or other forms of pretreatment depend upon the mixing process chosen. The muck feeder may be a weight conveyor, screw conveyor, batch weighing system, or positive displacement pump. This ensures that the sludge is added in correct proportions to the asphalt. Heated asphalt would be fed into the blender/mixer separately using a positive displacement, oil-type pump. The grade of asphalt used would depend upon the mixing temperature chosen. Once the sludge and heated asphalt have been combined satisfactorily, the encapsulated material may require an additional step involving heating for a longer interval to dewater and/or degrade components of the TNT sludge. Alternatively, if the mixing method itself provides sufficient time and temperature to degrade as well as encapsulate the sludge, the material can be discharged to containers or pumped to a storage pit/pond.

The operating rate and mixer size was evaluated in order to assess whether the sludge in the lagoon could be processed in a reasonable time frame using a portable mixer. Assuming a use of 50% asphalt to 50% wet sludge, a total of 730 m^3 (approximately 193,000 gallons) would be processed. Assuming a reasonable operating period of 24 days at 8 hours each, an average throughput of 20 gpm of encapsulated waste must be handled. This requires sludge and asphalt feed rates of 10 gpm. The amount of time required to achieve proper mixing plus the additional time (if any) at the temperature that is required to degrade the TNT is regarded as the system residence time. The residence time identifies the mixer and/or detention tank volume by the following computation.

Throughput (gpm) x Residence Time (min) = Tank Size (gal)

Residence Time (min)	Mixer/Tank Size (gal)
5	100
10	200
15	300
20	400

It is readily apparent that a residence time in excess of 20 minutes will require an impractically large tank. In this case two options are available. First, operate at lower throughput or second, consider the energy retained by the encapsulated sludge after discharge. Depending upon the size of casting or briquette used the encapsulated sludge may maintain a high temperature for hours.

Heating Requirements

A laboratory evaluation was conducted to assess the temperature and holding times required for

breakdown of the nitroaromatics and RDX in the sludge. This information is necessary to design the mixer system and to determine if thermal degradation occurs at temperatures below the flashpoint of available asphalts. A total of 17 heating tests were conducted, representing 4 temperatures (150, 200, 250, and 300° C) and 4 residence times (5, 10, 15, 20 minutes) plus one sample heated for 2 hours at boiling (100° C). For each test, 80 grams of sludge were placed in a 250 ml erlenmeyer flask. The flask was plugged with the teflon stopper and the thermocouple connections were made to the sludge. The flask was then placed in the preheated high temperature oven set to the end temperature desired. Temperature of the sludge was monitored throughout the test.

The samples of the heated sludge were sent to Envirodyne Engineers, Inc. for analysis of the nitroaromatics and RDX. The results are presented in Table 5. Although the sludge was homogenized prior to the heating experiment, variations in the concentrations were observed in the results. This phenomenon has occurred in most of the analytical work on these sludges and may be due to the presence of small particles of nearly pure TNT or foreign materials (sand, waxes, etc.) which cannot be completely homogenized. The results, however, do indicate that thermal degradation of approximately 90% of the explosive and nitroaromatic compounds occurs at 250° C. The results presented here are based solely on the heating of the sludge. Further testing will be required in order to determine whether various types of asphalt in combination with the sludge result in equally low levels of explosive and nitroaromatic compounds.

Conclusions

Asphalt encapsulation of pink water sludges using either a static or pug mill mixer appears to be a potential alternative to encapsulation by twin-screw extruders or other treatment techniques based on a preliminary evaluation of available mixers. The use of these mixers may reduce equipment costs and processing times for mobile systems. Heating experiments of pink water sludge not yet encapsulated indicated a 90% reduction in the levels of explosive and nitroaromatic compounds at a temperature of 250° C.

Pilot scale testing of the encapsulation system will be conducted prior to implementation in the field. The initial tests will use a synthetic sludge with physical properties similar to the pink water sludge. Modifications to the system and safety reviews will be completed prior to final pilot testing of the actual TNT-sludge. Additional laboratory tests on the asphalt-sludge mixture, perhaps heated to temperatures between 250° C and 300° C, may also be required to assess the leaching characteristics of the final product.

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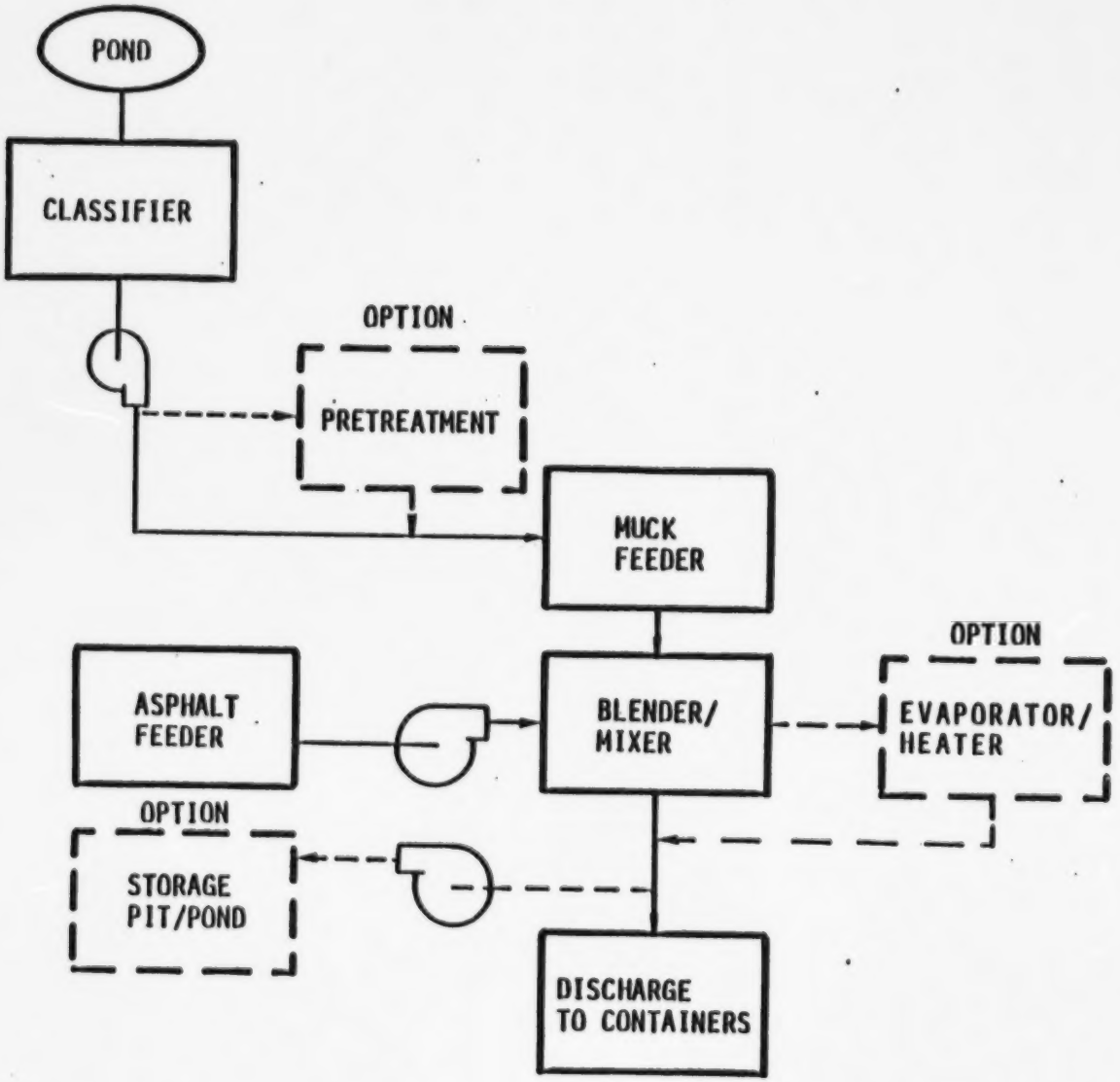

Figure 1. Sludge Encapsulation Process

TABLE 1: SUMMARY OF ANALYTICAL RESULTS, PINK WATER LAGOON

Parameter	Sludge	Soil Directly Beneath the Lagoon (sample depth less than 0.5 m)	Lagoon Water	Groundwater
Pink Water				
2,4,6-TNT	200 to 56,700 ppm	18.9 to 158 ppm	774 to 998 ppb	2900 to 6400 ppb
Tetryl	41.8 to 2100 ppm	.04 to 19.6 ppm	NA	NA
RDX	611 to 3740 ppm	35.7 to 91.6 ppm	19170 ppb	NA
2,4-DNT	.825 to 40.1 ppm	.04 to .180 ppm	1.1 ppb	113 to 185 ppb
2,6-DNT	.106 to .901 ppm	.04 to .173 ppm	1.1 ppb	10 to 19.5 ppb
Nitrobenzene	1.090 to 9.14 ppm	.05 to 1.78 ppm	11 ppb	11 ppb
1,3-Dinitrobenzene	.287 to 7.02 ppm	.04 to .29 ppm	1.8 ppb	135 to 173 ppb
Moisture[1]	49% to 92%	17% to 21%	NA	NA
pH	7.1 to 7.5	7.5 to 8.6	7.69	5.63 to 5.64
Reactivity	No	NA	NA	NA

NA: not determined

[1] % moisture = (g water/g sample) x 100

TABLE 2: MIXER CANDIDATES

Mixer	Industry Use	Type	Options
Pug Mill	Base Stabilization (soil mixing), Asphalt Paving Concretes, Portland Cement Concretes	Batch or Continuous	Spray Bar (liquid additions), Covers, Intake/Discharge Chutes, Heat Jacketing
Dryer-Drum	Portable Asphalt Concrete Plants	Continuous	Sealed drum, Bag House Raw Material Storage Conveyors, Asphalt Tank
Vertical Axis	Chemical: Abrasive, Corrosives, Explosives, Concretes, Clays	Batch	Muller & Plow Combinations, Dust Cover, Liquid Metering System, Renewable Pan Liners
Horizontal Axis	Food, Chemical: Pastes, Batter, Candy	Batch	Mixing Elements: Ribbon, Gate, Differential Screw. Heat Jacketing
Extruder	Plastics, Food, Waste Disposal.	Continuous	Heat Jacketing, Vapor Collection, Remote Controlling
Static	Chemical Processing, Fibrous Slurries, Explosives, Polymer Mixing, Liquid-Liquid or Liquid-Solid Mixing. Rubber, Paint Mixing, Food Mixing	Continuous	Heat Jacketing

TABLE 3: MIXER SELECTION MATRIX

MIXER / CRITERION	PUG MILL (STABILIZER)	DRYER DRUM	VERTICAL AXIS (PLANETARY, COUNTER-CURRENT	HORIZONTAL AXIS (RIBBON, GATE, DOUBLE-SCREW)	EXTRUDER	STATIC
Degree of Mixing	Mod-High	Low	Mod-High	Mod-High	High	Mod
Provision for Loading/ Discharging Materials	Exists	Exists	Requires Design	Requires Design	Exists	Requires Design
Field Worthiness	Rugged	Rugged	Requires Weather-proofing	Requires Weather-proofing	Requires Weather-proofing	Requires Weather-proofing
Heat Capabilities	Heat Jacket is Common Option	Exists	Requires Addition of Heat Jacket	Heat Jacket Available for Some Types	Exists	Requires Addition of Heat Jacket
Handles all Sludge Consistencies	Yes	Cannot Use a Slurry	Yes	Yes	Yes	Must Use a Slurry
Portability	Yes	Yes	Trailer mounting req'd. Many are not practical to use in field	Trailer mounting req'd. Many are not practical to use in field	Trailer Mounting Required	Trailer Mounting Required
Cost	Low	Mod	Mod	Mod	High	Very Low
Overall Complexity	Low	Low	Mod	Mod	High	Low

TABLE 4: ASPHALT TYPES

Type	Viscosity Range	Uses	Pure Asphalt %	Use Temp °C	ASTM Minimum Flash Point** °C
Blown Asphalt (oxidized) ASTM D312	—	Steep Roofing, Pipe Coating Under Sealing, Cavity Filling Waterproofing	100	135° (min)	225° (min)
Asphalt Cement ASTM D946 ASTM D3381 Penetration & Viscosity Graded	80-550 Centistokes at 275°F	Plant-Made Asphalt Concrete for Roads, Sidewalks, Parking Lots, Dam Facings, Penetration Macadam.	100	82°-176°	163°-238° (min)
Cutback Asphalt Rapid Medium curing Slow ASTM D2028, D2027 D2026	30-6000 Centistokes at 140°F	Road Mixing of Asphalt Concretes. Asphalt Penetration Applications. Prime & Tack Coats Before Paving. Stockpiled Patching Mixes.	50-80	57°-116°**	RC-27° MC-38°-66° SC-66°-107°
Emulsified Asphalts Rapid Medium setting Slow ASTM D977, D2397	20-100 Saybolt Seconds at 77°F	Seal Coating. Penetration Macadam. Road Mixing of Asphalt Concretes. Fine Aggregate or Soil Stabilization. Cold or Hot Plant Mixing. Patching Mixes.	55-65	10°-71°	Will Not Flash

*Flash points of specific products may exceed the minimum required by ASTM for that category.
**Application temperature may exceed flash point. Caution must be exercised.

TABLE 5: CONCENTRATIONS OF NITROAROMATICS, TETRYL AND RDX IN HEATED SLUDGE SAMPLES (ppm, dry weight basis)

Sample No.	Temperature (°C)	Holding Time (min)	2,4,6-TNT	RDX	Tetryl	NB*	1,3-DNB*	2,6-DNT*	2,4-DNT*	1,3,5-TNB*
1	150°C	5	39,750	604	2730	0.7	0.55	126	209	0.6
2		10	62,690	470	5050	0.7	0.55	104	190	0.6
3		15	31,210	495	16,000	0.7	0.55	69	194	0.6
4		20	31,670	668	11,300	0.7	13	83	190	0.6
5	200°C	5	15,850	779	2780	0.7	14	76	151	0.6
6		10	7180	862	390	0.7	29	42	154	0.6
7		15	23,660	974	5260	0.7	13	94	206	0.6
8		20	22,680	926	3220	0.7	13	115	235	0.6
9	250°C	5	2300	362	4140	0.7	20	57	86	91
10		10	3500	357	23	0.7	19	71	106	95
11		15	3240	485	19	0.7	27	89	137	125
12		20	1740	685	19	0.7	26	62	117	122
13	300°C	5	35	10	(b)	0.7	3	6.9	7.5	6.4
14		10	3.6	29	1	0.7	0.55	0.42	0.48	0.6
15		15	5.6	0.85	1	0.7	0.55	0.42	0.48	0.6
16		20	1.5	0.85	1	0.7	0.55	0.42	0.48	0.6
17	100°C	120	42,360	300	43,760	0.7	0.55	0.42	33	0.6
17 Dupl		120	43,320	314	—	0.7	0.55	0.42	37	0.6
Method Blank	—	—	0.47	0.85	1	0.7	0.55	0.42	0.48	0.6

*NB = nitrobenzene
DNB = dinitrobenzene
DNT = trinitrotoluene
TNB = trinitrobenzene

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